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(54) **ABSORBENT GLASS MAT BATTERY**

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CPC **H01M 50/44** (2021.01); **H01M 4/14** (2013.01); **H01M 4/5825** (2013.01);
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(58) **Field of Classification Search**

CPC H01M 50/431; H01M 50/44; H01M 2220/20; H01M 4/73; H01M 4/14
See application file for complete search history.

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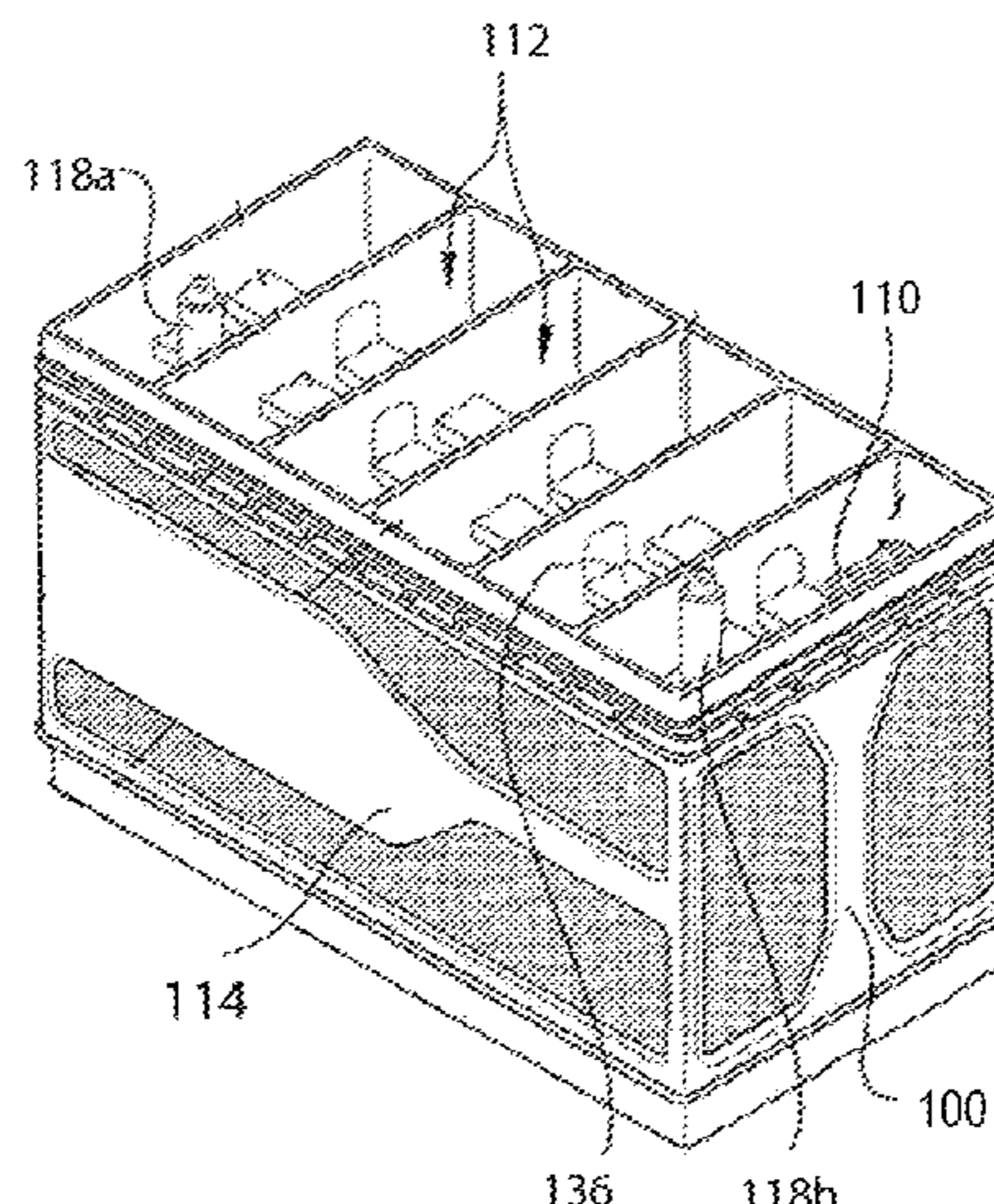
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(57) **ABSTRACT**

A lead-acid battery is disclosed. The lead-acid storage battery has a container with a cover, the container including one or more compartments. One or more cell elements are provided in the one or more compartments. The one or more cell elements include a positive plate, the positive plate having a positive grid and a positive electrochemically active material on the positive grid; a negative plate, the negative plate having a negative grid and a negative electrochemically active material on the negative grid, wherein the negative electrochemically active material comprises barium sulfate and an organic expander; and a separator between the positive plate and the negative plate. Electrolyte is provided within the container. One or more terminal posts
(Continued)



extend, from the cover and are electrically coupled to the one or more cell elements.

20 Claims, 11 Drawing Sheets

Related U.S. Application Data

(60) Provisional application No. 62/661,444, filed on Apr. 23, 2018, provisional application No. 62/584,499, filed on Nov. 10, 2017, provisional application No. 62/530,718, filed on Jul. 10, 2017, provisional application No. 62/517,737, filed on Jun. 9, 2017.

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H01M 4/58 (2010.01)
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H01M 10/08 (2006.01)
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H01M 50/543 (2021.01)
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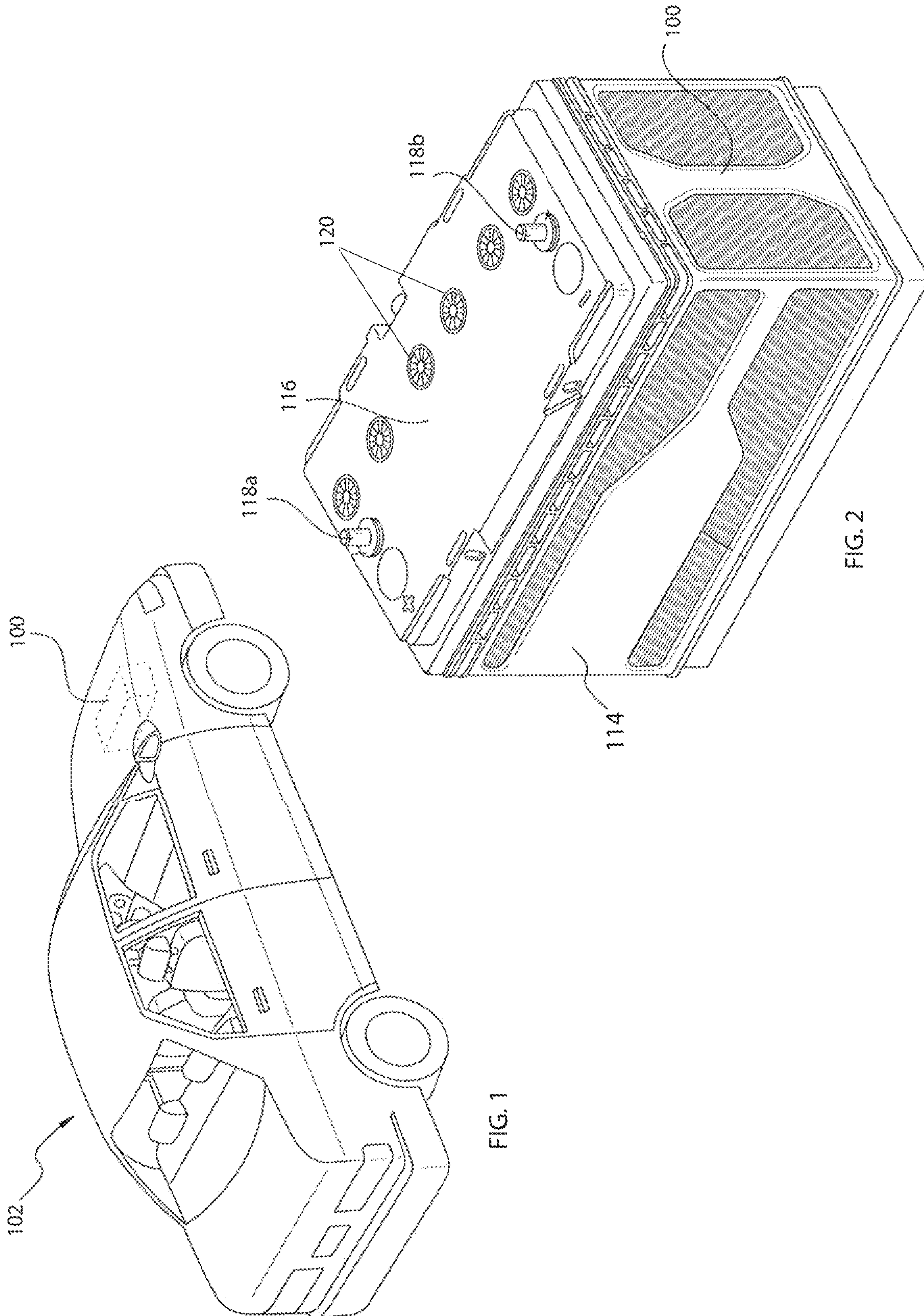
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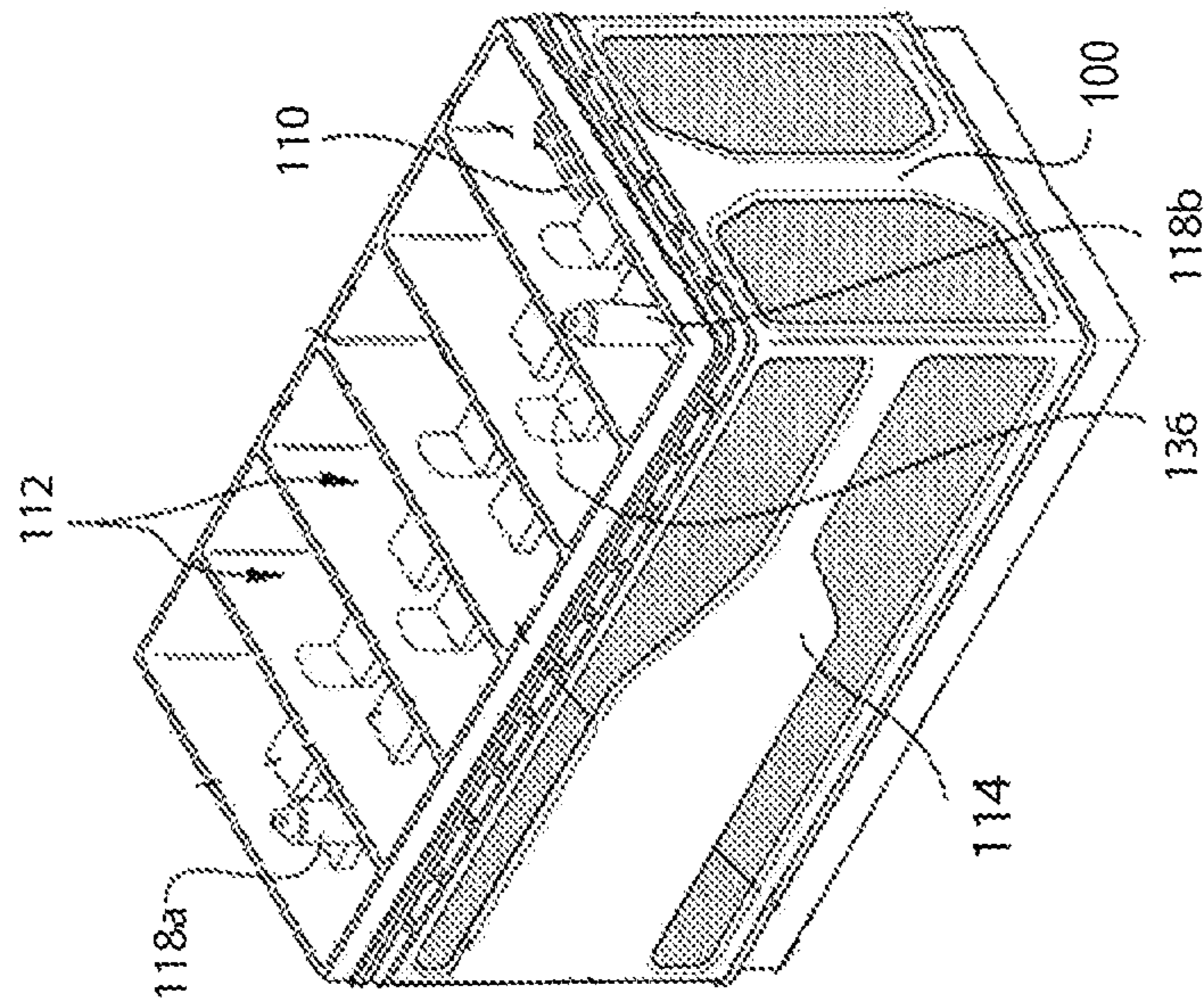


FIG. 3

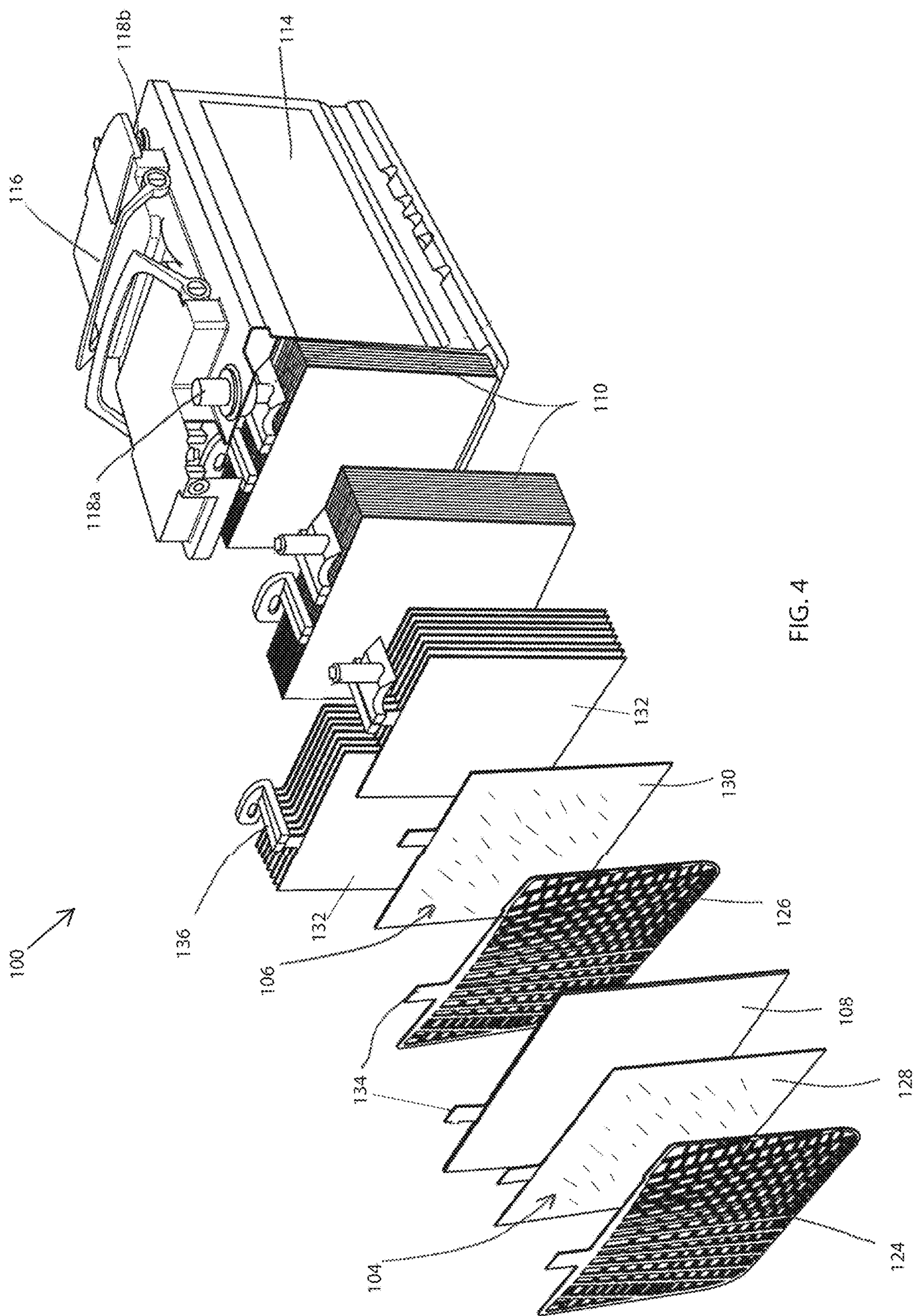
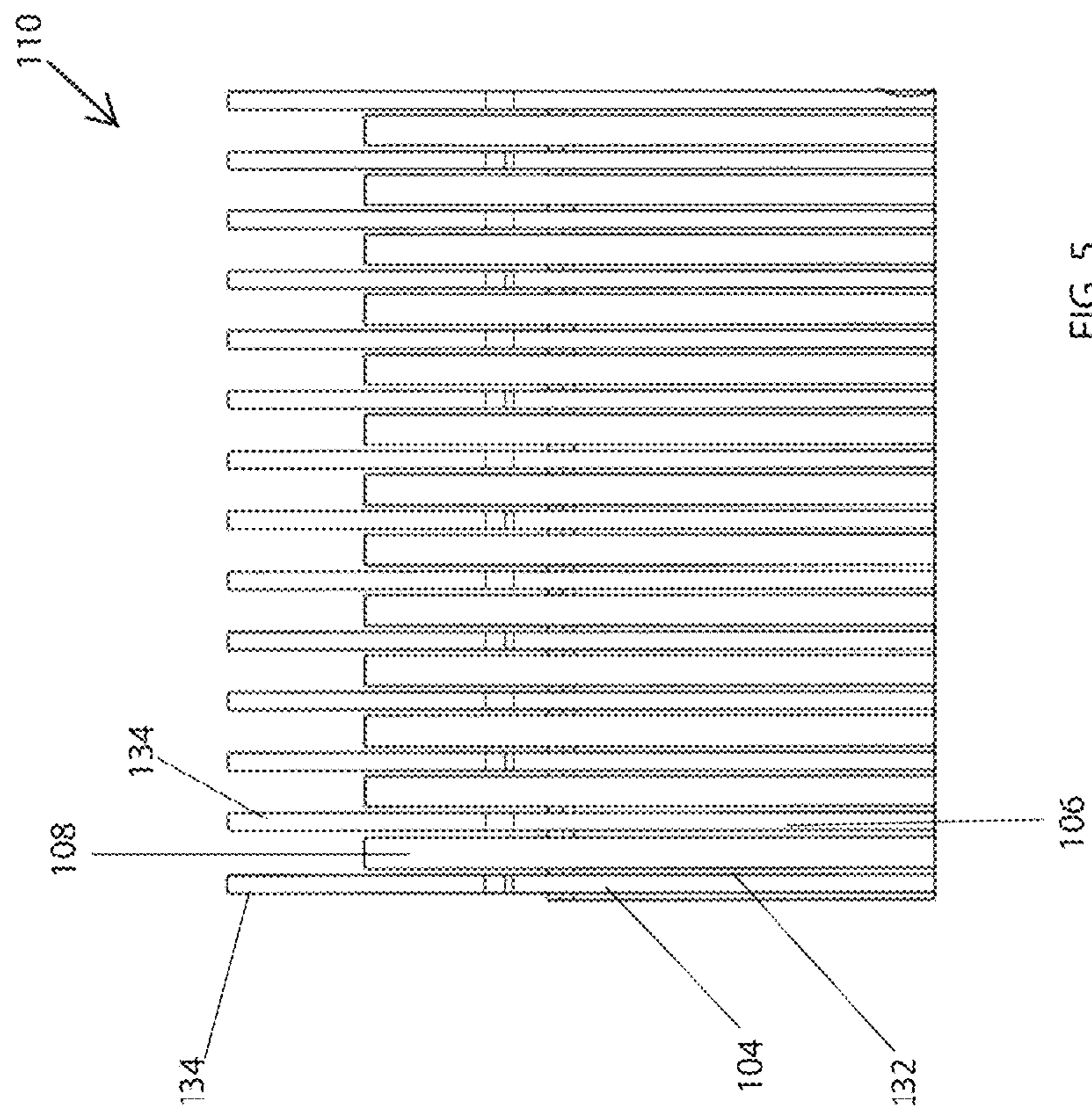


FIG. 4



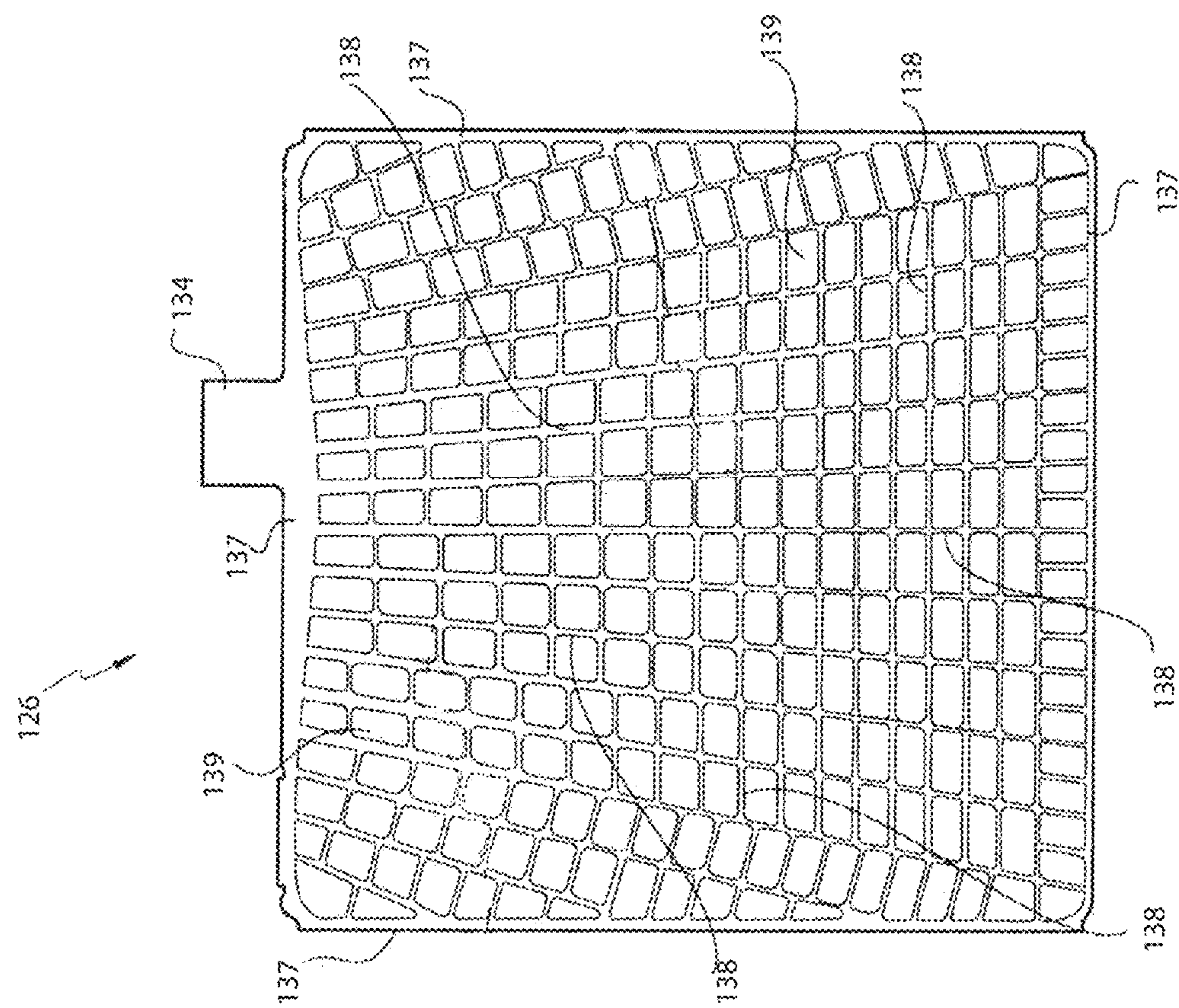


FIG. 6

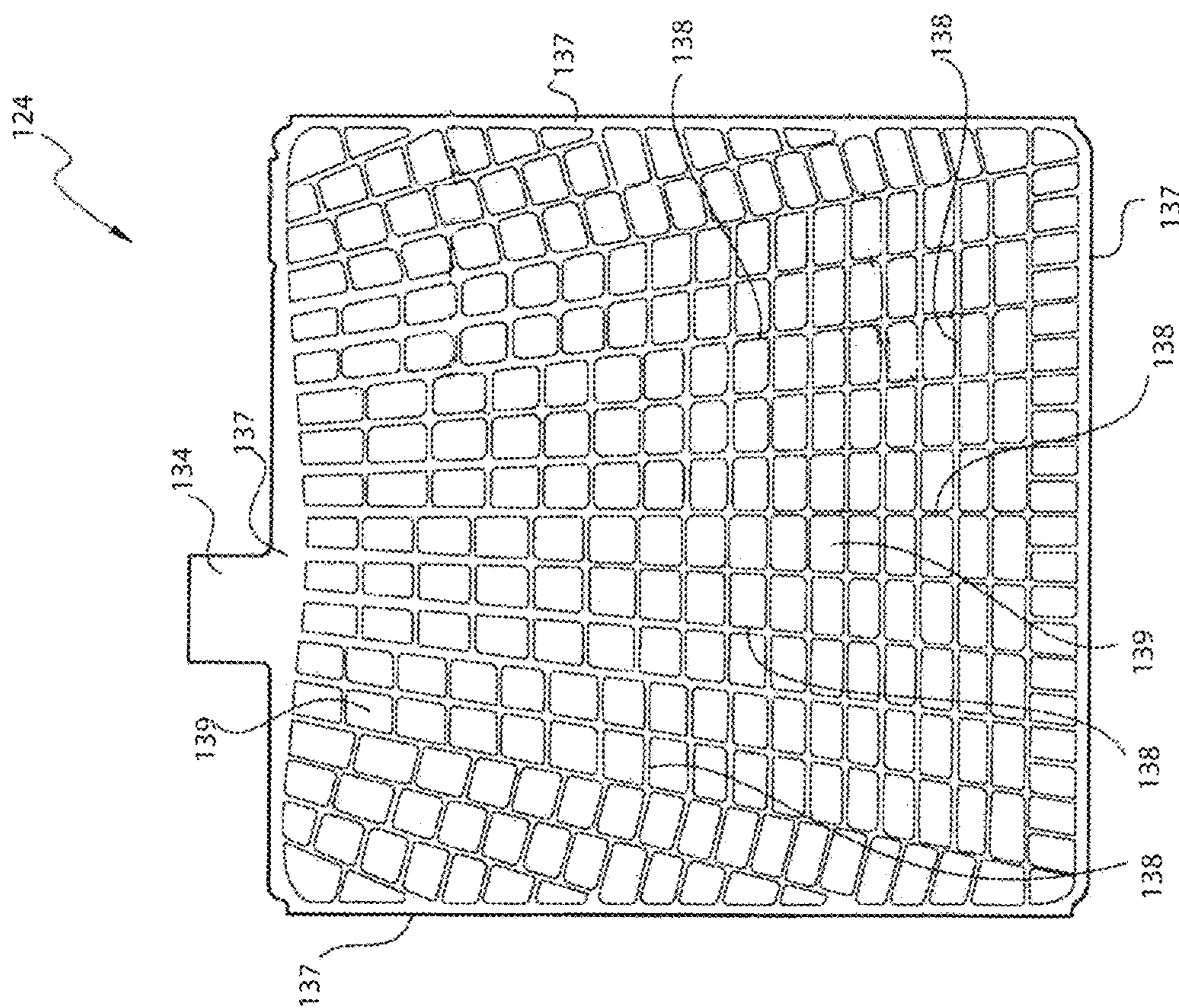


FIG. 7

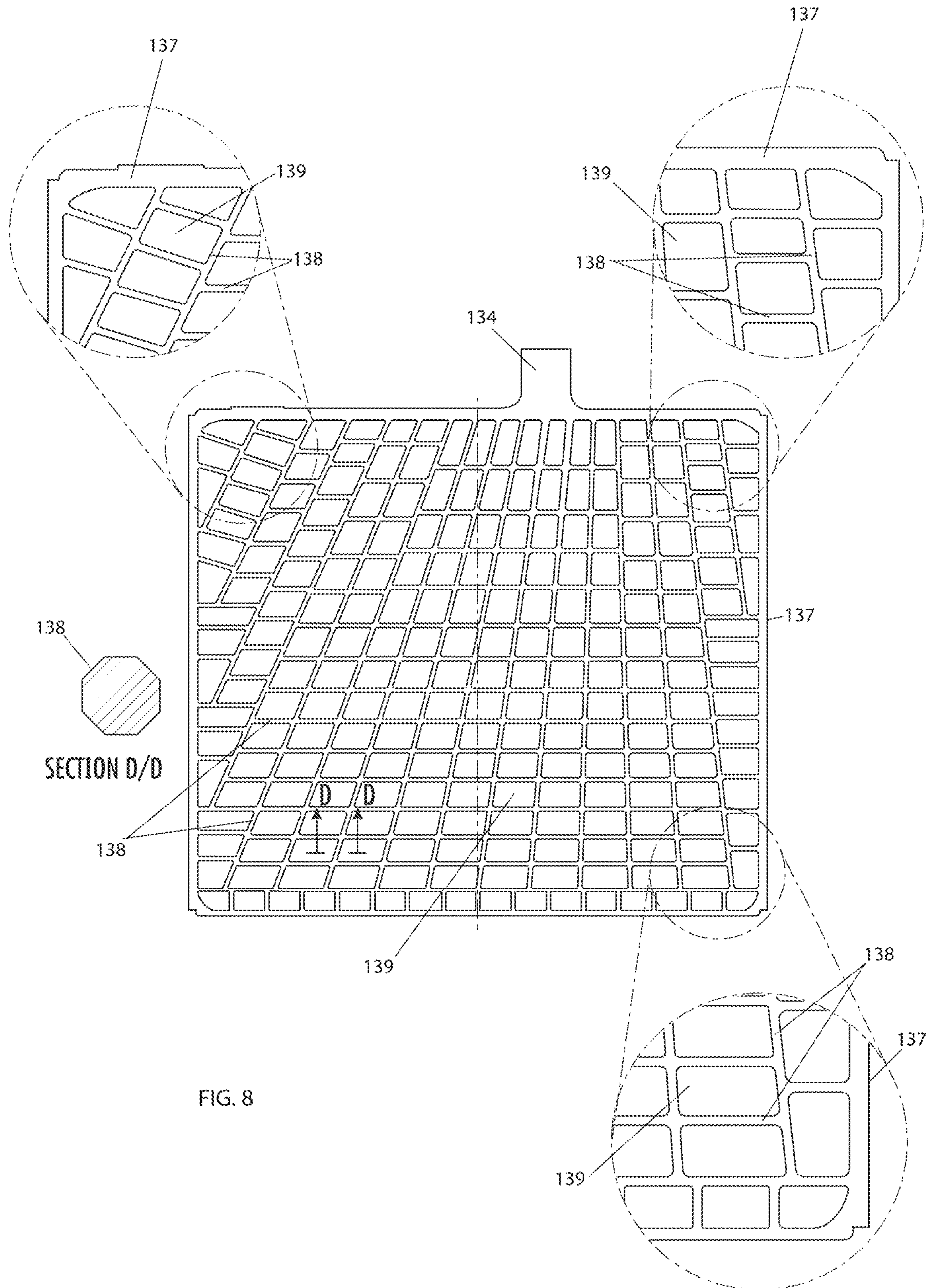
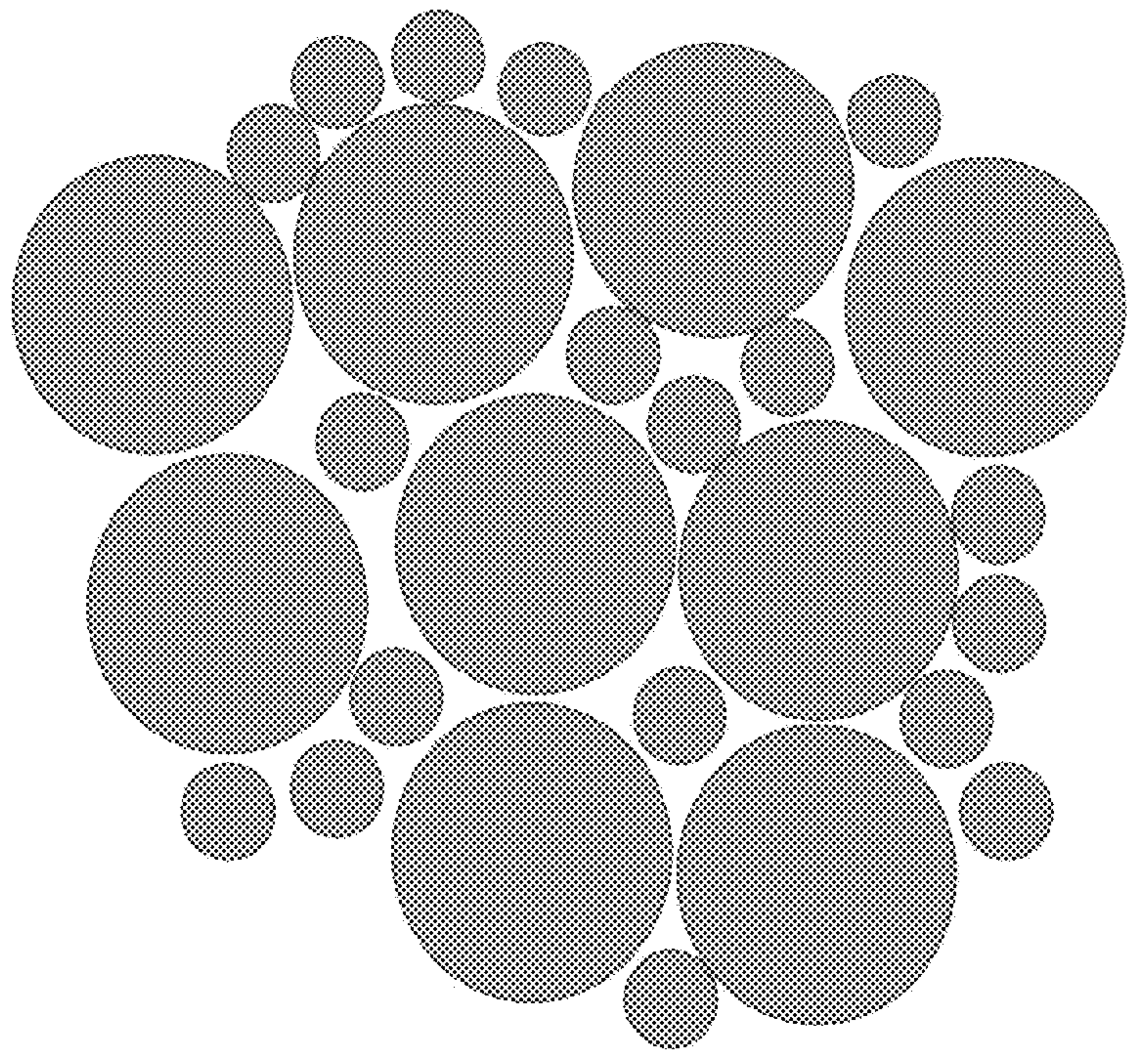
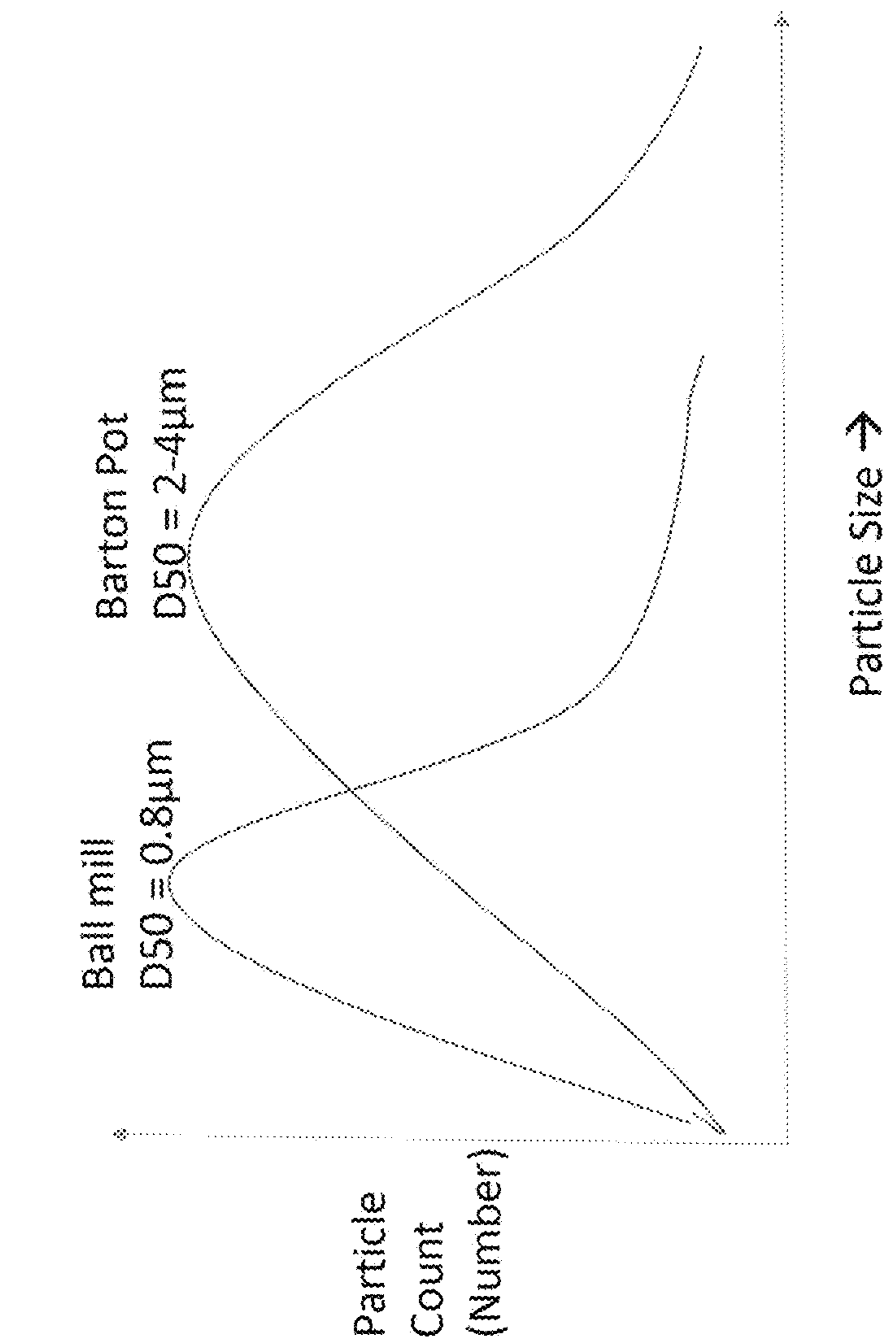


FIG. 8

Oxide Particle Size distribution – bimodal distribution

FIG. 9



Packing Example – large and small together

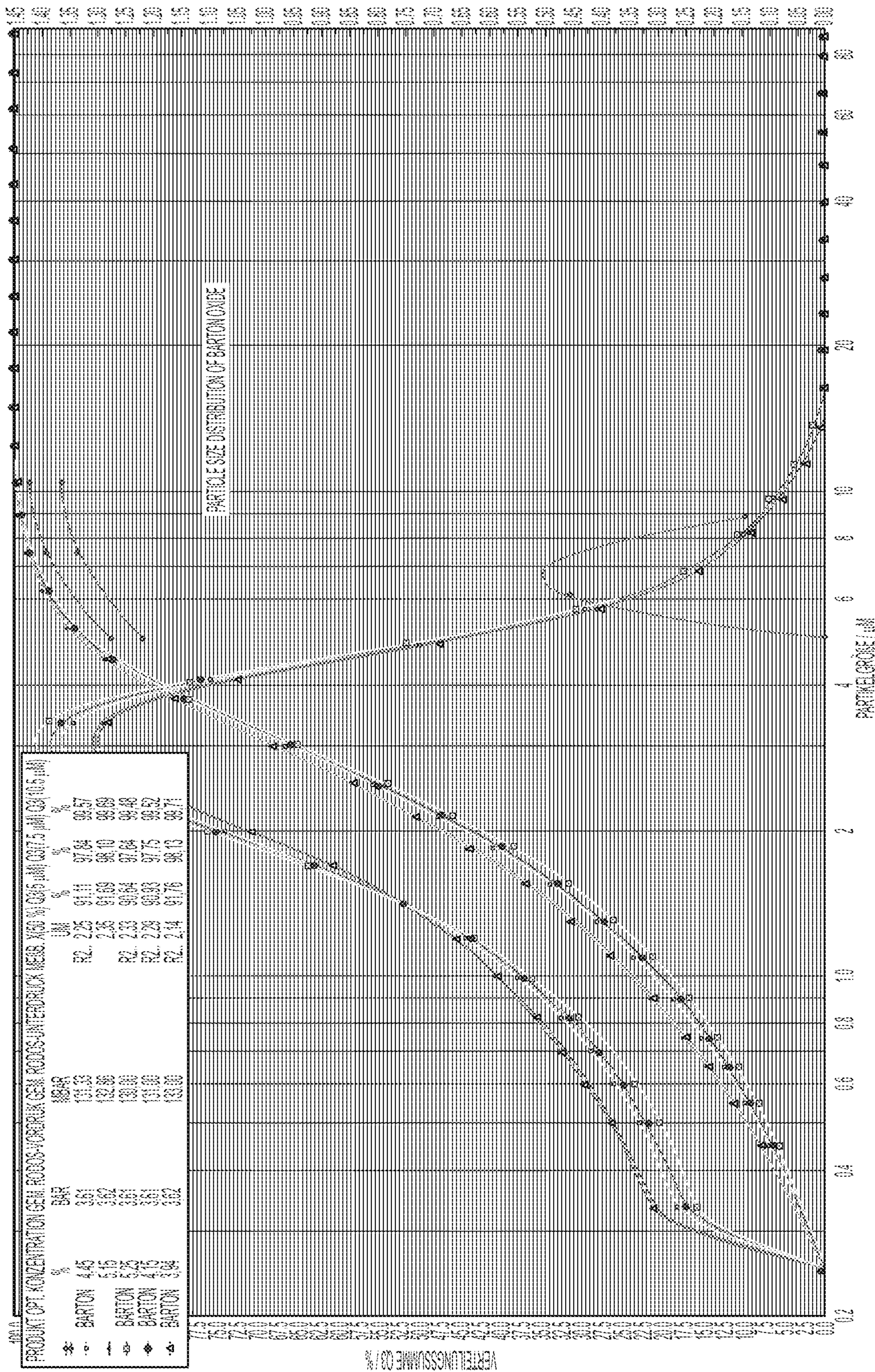


FIG. 10

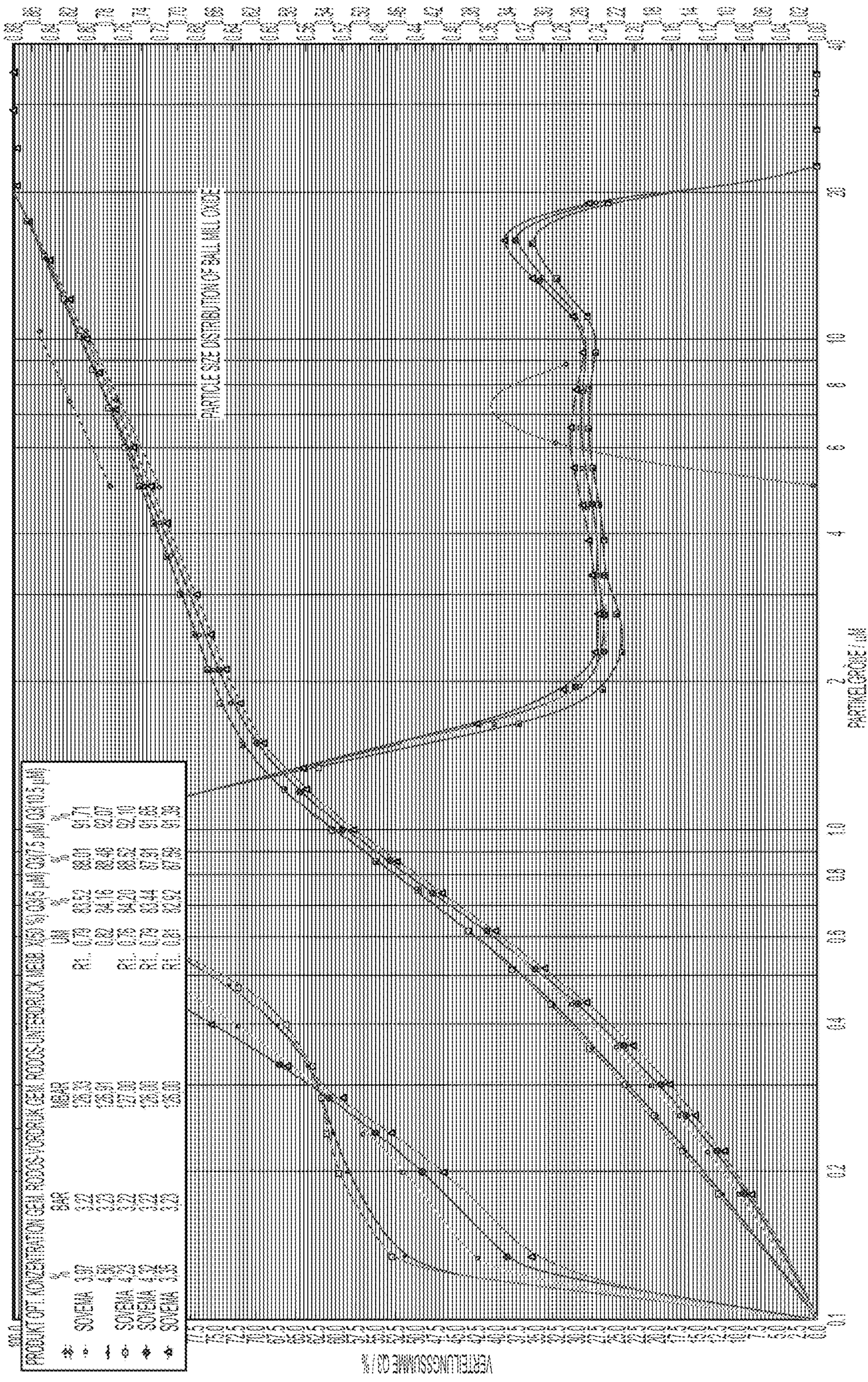


FIG. 11

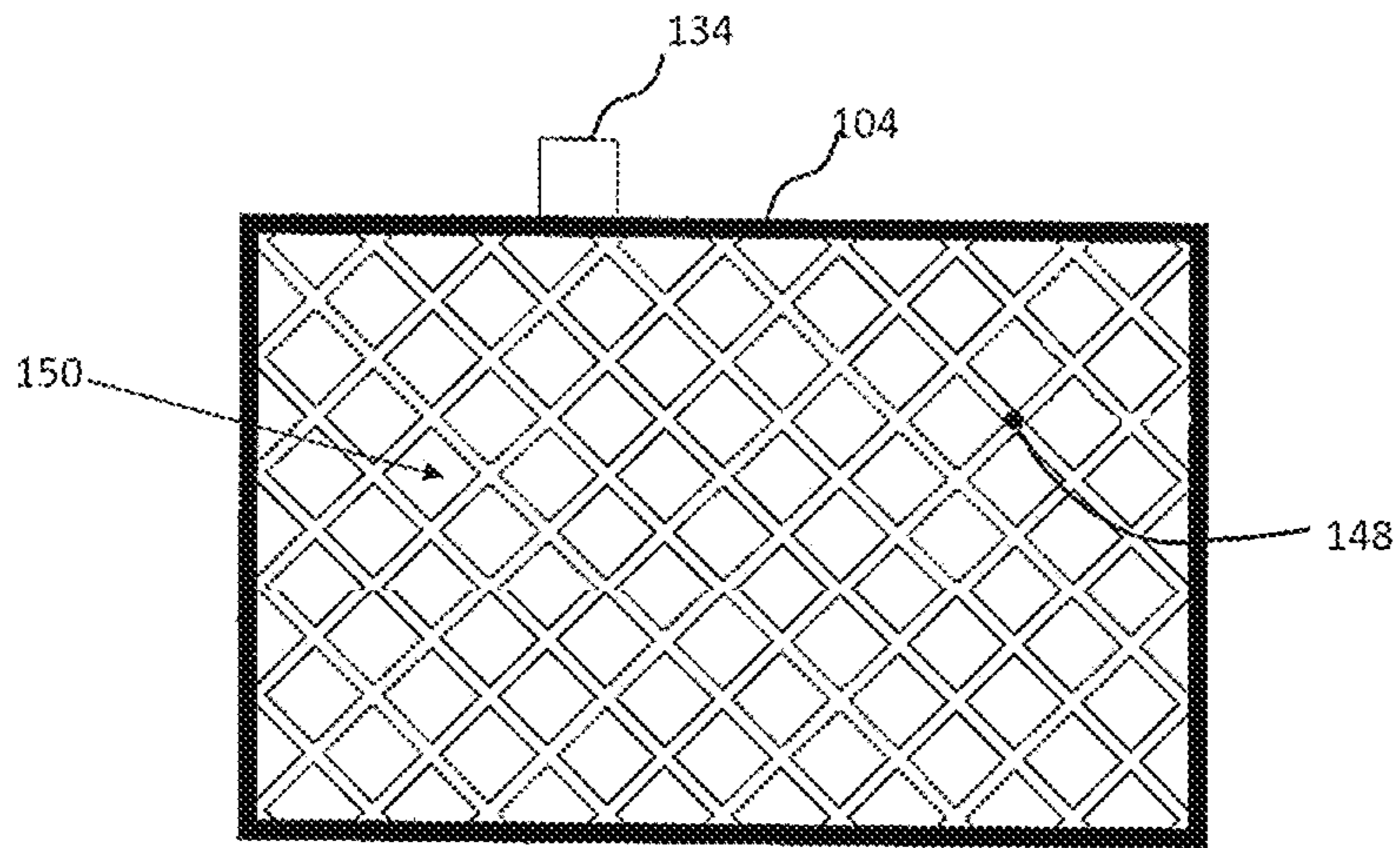


FIG. 12

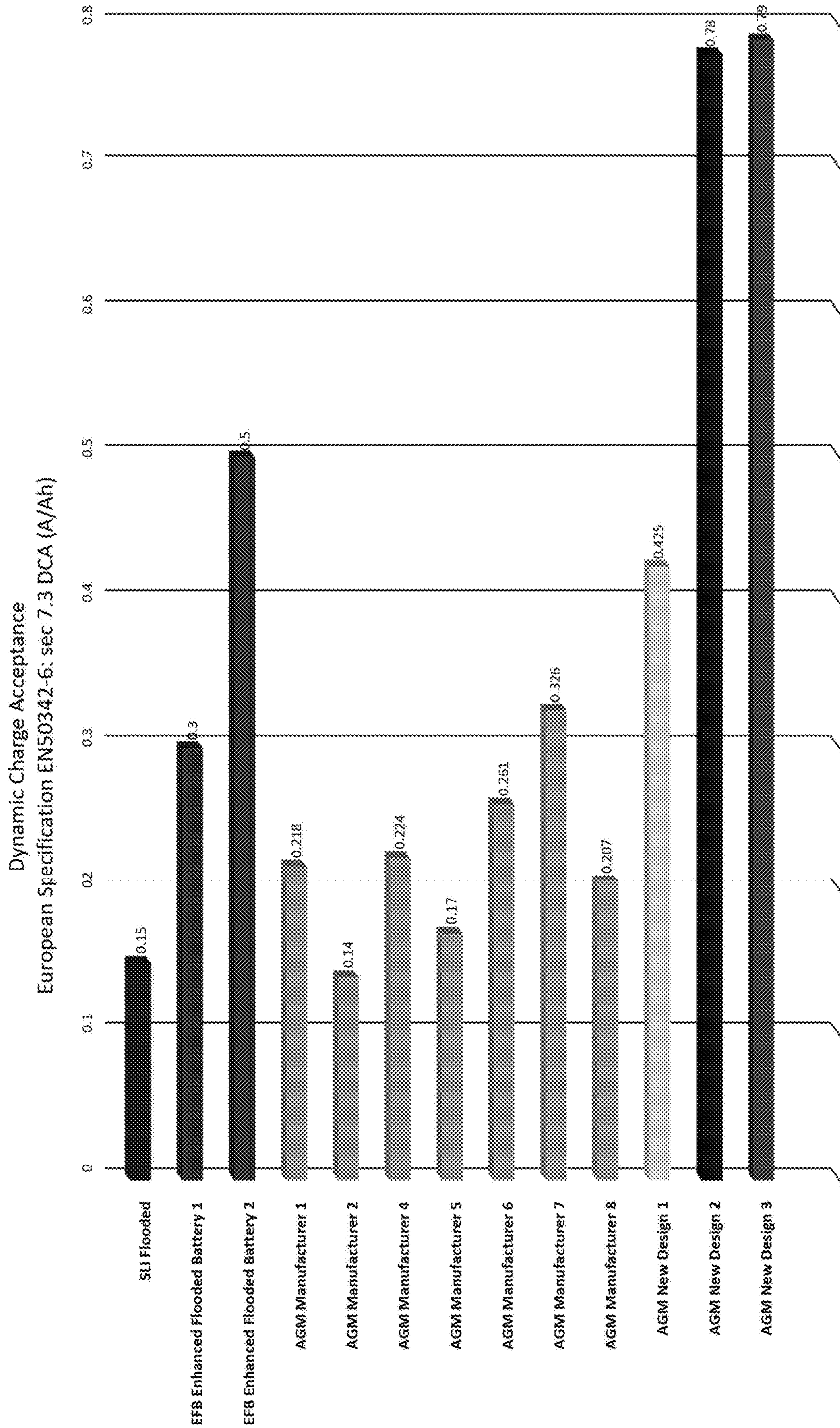


FIG. 13

ABSORBENT GLASS MAT BATTERY**CROSS-REFERENCE. TO RELATED APPLICATIONS**

This application is a Continuation of U.S. patent application Ser. No. 16/620,299, filed Dec. 6, 2019, entitled "ABSORBENT GLASS MAT BATTERY", issued Aug. 9, 2022 as U.S. Pat. No. 11,411,280; which is a National Stage Entry of PCT/US2018/036767, filed Jun. 8, 2018, entitled "LEAD-ACID BATTERY"; which claims priority to U.S. Provisional Patent Application No. 62/517,737, filed Jun. 9, 2017, entitled IMPROVED ABSORBENT GLASS MAT BATTERY; U.S. Provisional Patent Application No. 62/530,718, filed Jul. 10, 2017, entitled IMPROVED ABSORBENT GLASS MAT BATTERY, U.S. Provisional Patent Application No. 62/584,499, filed Nov. 10, 2017, entitled IMPROVED ABSORBENT GLASS MAT BATTERY, and U.S. Provisional Patent Application No. 62/661,444, filed Apr. 23, 2018, entitled IMPROVED ABSORBENT GLASS MAT BATTERY, the entire contents of each of which are incorporated by reference herein in their entireties.

FIELD

The present inventions relate to the field of batteries. The present inventions more specifically relate to the field of lead-acid batteries.

BACKGROUND

Lead-acid batteries are known. Lead-acid batteries are made up of plates of lead and separate plates of lead dioxide, which are submerged into an electrolyte solution. The lead, lead dioxide and electrolyte provide a chemical means of storing electrical energy which can perform useful work when the terminals of a battery are connected to an external circuit.

One type of lead-acid battery is an AGM or absorbent glass mat lead-acid battery which is a sealed (e.g., maintenance-free), or more specifically a valve regulated battery, in which the electrolyte is absorbed and retained in a mat that is wrapped around or interleaved with an electrode(s) or plate(s). AGM lead-acid batteries are recombinant batteries, that is, H₂ and O₂ generated during charging are recombined to water in the battery.

AGM lead-acid batteries are advantageous over traditional starting, lighting and ignition (SLI) batteries, in that they are better suited to providing power in a vehicle with numerous electronic features or plug-in accessories. AGM batteries are also a preferred solution for fuel saving start-stop vehicle technology.

Start-stop vehicles can place various demands on a battery. Vehicles also are increasing in the electrical load of components, for which the electrical load must be supported through a stop event. Vehicle manufacturers are seeking a cost effective, reliable energy storage solution that ensures a seamless customer experience. Therefore there is a need for consistent reliable performance from a lead-acid battery. There is also a need for a robust battery which can support additional prolonged/intermittent loads and support optimal duration and frequency of stop events. To this end, a need exists for a lead-acid battery which provides sustainable and fast rechargeability (e.g., optimized charge acceptance) and consistent cycling performance. Accordingly, a need exists for an AGM lead-acid battery with improved performance over existing devices.

SUMMARY

A lead-acid storage battery and an absorbent glass mat lead-acid storage battery are disclosed which have improved performance.

More specifically, a lead-acid battery is disclosed. The lead-acid battery has a container with a cover and includes one or more compartments. One or more cell elements are provided in the one or more compartments. Each cell element includes a positive plate, the positive plate having a positive grid and a positive electrochemically active material on the positive grid; a negative plate, the negative plate having a negative grid and a negative electrochemically active material on the negative grid, wherein the negative electrochemically active material comprises, in part, barium sulfate and an expander; and an absorbent glass mat separator between the positive plate and the negative plate. Electrolyte is provided within the container. One or more terminal posts extend from the container or the cover and are electrically coupled to the one or more cell elements.

Another lead-acid storage battery is disclosed having a container with a cover, the container including one or more compartments. One or more cell elements are provided in the one or more compartments. The one or more cell elements include a positive plate, the positive plate having a positive grid and a positive electrochemically active material on the positive grid; a negative plate, the negative plate having a negative grid and a negative electrochemically active material on the negative grid, wherein the negative electrochemically active material comprises, in part, barium sulfate and an expander; and a separator between the positive plate and the negative plate. Electrolyte is provided within the container. One or more terminal posts extend from the container or the cover and are electrically coupled to the one or more cell elements.

A further lead-acid storage battery is disclosed. The battery comprises a container with a cover, the container including one or more compartments and one or more cell elements in the one or more compartments. The one or more cell elements have a positive plate, the positive plate having a positive grid and a positive electrochemically active material on the positive grid; a negative plate, the negative plate having a negative grid and a negative electrochemically active material on the negative grid; wherein the negative electrochemically active material comprises, in part, one or more carbons (carbonaceous materials), barium sulfate, and one or more expanders; and an absorbent glass mat separator between the positive plate and the negative plate. Electrolyte is provided within the container, wherein the electrolyte comprises a sulfuric acid solution including one or more metal sulfates, wherein the metal sulfates are soluble metal sulfates selected from the group consisting of the elements Al, Mg, Na, K, Li, and Zn. One or more terminal posts extend from the container or the cover and are electrically coupled to the one or more cell elements.

These and other features and advantages of devices, systems, and methods according to this invention are described in, or are apparent from, the following detailed descriptions of various examples of embodiments.

BRIEF DESCRIPTION OF DRAWINGS

Various examples of embodiments of the systems, devices, and methods according to this invention will be described in detail, with reference to the following figures, wherein:

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FIG. 1 is a perspective view of a vehicle for use with an absorbent glass mat battery according to one or more examples of embodiments described herein.

FIG. 2 is a perspective view of an absorbent glass mat battery according to one or more examples of embodiments described herein.

FIG. 3 is a perspective view of the absorbent glass mat battery shown in FIG. 2, with the cover removed.

FIG. 4 is an exploded perspective view of an absorbent glass mat battery according to one or more examples of embodiments described herein.

FIG. 5 is a partial, side elevation view of a cell element according to one or more examples of embodiments for use with the absorbent glass mat battery shown in FIG. 2.

FIG. 6 is an elevation view of an example battery grid for use with the absorbent glass mat battery shown in FIG. 2.

FIG. 7 is an additional elevation view of an example battery grid for use with the absorbent glass mat battery shown in FIG. 2.

FIG. 8 is an elevation view of an alternative example battery grid for use with the absorbent glass mat battery shown in FIG. 2, showing section details of the illustrated grid.

FIG. 9 is an example illustration of a bimodal particle size distribution of oxide.

FIG. 10 is an example particle size distribution of oxide produced by Barton Pot method.

FIG. 11 is an example particle size distribution of oxide produced by Ball Mill method.

FIG. 12 is an elevation view of one or more examples of a plate having an imprint on the plate surface.

FIG. 13 is a graph showing performance data, namely, dynamic charge acceptance, of a battery of the type described herein compared to existing batteries.

It should be understood that the drawings are not necessarily to scale. In certain instances, details that are not necessary to the understanding of the invention or render other details difficult to perceive may have been omitted. It should be understood, of course, that the invention is not necessarily limited to the particular embodiments illustrated herein.

DETAILED DESCRIPTION

Referring to the Figures, a battery 100 is disclosed, and in particular a rechargeable battery, such as, for example, a lead-acid battery. According to one or more examples of embodiments, the battery 100 is a lead-acid storage battery. Various embodiments of lead-acid storage batteries may be either sealed (e.g., maintenance-free) or unsealed (e.g., wet). According to one or more examples of embodiments, the lead-acid storage battery 100 is preferably a sealed lead-acid battery or AGM lead-acid battery and, to this end, may include an absorbent glass mat 108 (referred to interchangeably herein as "AGM"). While specific examples are described and illustrated, the battery 100 may be any secondary battery suitable for the purposes provided.

A battery 100 is provided and shown in a vehicle 102 in FIG. 1. Referring to FIGS. 2-5, the battery 100 is an AGM lead-acid battery having positive and negative plates 104, 106 which are separated by an absorbent glass mat 108 that absorbs and holds the battery's acid or electrolyte and prevents it from flowing freely inside the battery 100. The working electrolyte saturation is at some value below 100% saturation to allow recombinant reactions of hydrogen and oxygen. The AGM lead-acid battery 100 includes several cell elements 110 which are provided in one or more

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separate compartments 112 of a container or housing 114. The element stack 110 may be compressed during insertion reducing the thickness of the separator 108. A cover 116 is provided for the container or housing 114 and may be sealed to the container 114. In various embodiments, the container 114 and/or cover 116 includes battery terminals 118. The battery cover 116 may also include one or more filler hole caps and/or vent assemblies 120 (see FIG. 2).

Referring to FIG. 4, the plates 104, 106 include electrically-conductive positive or negative grids 124, 126 or current collecting members. Positive paste 128 is provided on the positive grid 124 and negative paste 130 is provided on the negative grid 126. More specifically, the positive plate 104 includes a positive grid 124 having or supporting a positive active material or paste 128 thereon, and in some examples of embodiments may include a pasting paper or a woven or non-woven sheet material comprised of fibers (e.g., a "scrim") 132; and the negative plate 106 includes a negative grid 126 having or supporting a negative active material or paste 130 thereon, and in some examples of embodiments may include a pasting paper or scrim 132. Positioned between the positive and negative plates 104, 106 is a separator 108. In a retained electrolyte-type battery 100 such as described herein, the separator 108 may be a porous and absorbent glass mat (AGM). In some examples, the absorbent glass mat 108 may also be used with an additional separator (not shown); various common commercially available separators are known in the art.

A plurality of positive plates 104 and a plurality of negative plates 106 (with separators 108) generally make up at least a portion of the electrochemical cell 110 (see FIGS. 3-5). As indicated, each plate set or cell 110 may include one or more positive plates 104 and one or more negative plates 106. Thus, the battery 100 includes a positive plate 104 and a negative plate 106, and more specifically a plurality of positive plates 104 and a plurality of negative plates 106. Referring to FIGS. 3-4, a plurality of plate sets or books or cell elements 110 may be electrically connected, e.g., electrically coupled in series or other configuration, according to the capacity of the lead-acid storage battery 100. Each grid has a lug 134 (see FIGS. 4-8). In FIGS. 3-4, one or more cast-on straps or intercell connectors 136 are provided which electrically couple the lugs 134 of like polarity in a plate set or cell element 110 and to connect other respective plate sets or cell elements 110 in the battery 100. One or more positive terminal posts 118a and one or more negative terminal posts 118b (FIGS. 2-4) may also be provided. Such terminal posts 118 typically include portions which may extend through the cover and/or container wall, depending upon the battery design. It will be recognized that a variety of terminal arrangements are possible, including top, side, front or corner configurations known in the art.

A plurality of positive plates 104 and negative plates 106 may be provided in stacks or plate sets or cell elements 110 for producing a battery having a predetermined voltage, for example a 12-volt battery in a vehicle 102. The number of cell elements 110 or plate groups or plate sets may be varied. It will also be obvious to those skilled in the art after reading this specification that the size and number of plates 104 and/or 106 in any particular group (including the size and number of the individual grids), and the number of groups used to construct the battery 100 may vary depending upon the desired end use.

As described in various embodiments herein, the positive and negative plates 104, 106 are paste-type electrodes (FIG. 4). Thus, each plate 104, 106 comprises a grid 124, 126 pasted with active material 128, 130. More specifically, the

paste-type electrode includes a grid which acts as a substrate and an electrochemically active material or paste is provided on the substrate. The grids, including a positive grid **124** and a negative grid **126**, provide an electrical contact between the positive and negative active materials or paste **128**, **130** which may serve to conduct current.

Referring to FIGS. **6-8**, in one or more examples of embodiments, the grids **124**, **126** may be the same or similar. To this end, the grids **124**, **126** may be stamped or punched fully framed grids having a frame **137** and a radial arrangement of grid wires **138** forming a pattern of open spaces **139**. In one example, both the positive grids **124** and the negative grids **126** may have such an arrangement. However, it is contemplated that the grids **124**, **126** may differ. For example, the positive grid **124** may be a stamped or punched fully framed grid having a radial arrangement of grid wires **138** and the negative grid **126** may be concast or, for example, expanded metal or gravity cast. Various examples of grids **124**, **126** suitable for use with the inventions described herein are shown and described in U.S. Pat. Nos. 5,582,936; 5,989,749; 6,203,948; 6,274,274; 6,953,641 and 8,709,664, which are hereby incorporated by reference herein. While specific examples of grid wire **138** arrangements and grid types are described for purposes of example, the invention is not limited thereto and any grid structure or arrangement suitable for the purposes of the battery **100** may be substituted in place of the described grids **124**, **126**. For example, a negative grid **126** having a different or improved profile may be provided. In one or more examples of embodiments, a negative grid **126** having a profile similar to that shown in U.S. Pat. No. 9,130,232, which is hereby incorporated by reference herein (and also shown in FIG. **8**), may be provided. In other examples of embodiments, the grid may be a punched grid, a continuously cast (concast) grid, an expanded metal grid, and so forth. In some examples of embodiments, the grid may also include surface roughening or may be subjected to one or more different surface treatments (e.g., solvent, surfactant and/or steam cleaning), such as may be used to improve paste adhesion among other benefits.

According to one or more examples of embodiments, the grid **124** material may be composed of lead (Pb) or a lead alloy (or any suitable conductive substrate, i.e. carbon fiber). The negative grid **126** may be composed of the same or similar material to the positive grid **124**. It is contemplated, however, that material composition may also vary between the positive grid **124** and the negative grid **126**. In one example of embodiments, the positive and negative grids **124**, **126** may also be formed of different thickness. However, it is contemplated that the grids **124**, **126** may be of the same thickness. The thickness of each grid may be varied based upon desired manufacturing and performance parameters. For instance, thickness may be determined based upon manufacturing requirements, such as for instance, minimum requirements for paste adhesion, or other suitable parameters. While specific examples are provided for purposes of illustration, variations thereon may be made to provide grid dimensions suitable for the particular application.

In more detail, the positive plate **104** contains a metal (e.g., lead or lead alloy) grid **124** with lead dioxide active material or paste **128** thereon. Examples of lead-containing compositions which may be employed in the positive paste **128** include, but are not limited to, finely-divided elemental Pb, PbO (“litharge” or “massicot”), Pb₃O₄ (“red lead”), PbSO₄ (“Lead sulfate” with the term “PbSO₄” being defined to also include its associated hydrates, and basic sulfates: 1PbO·PbSO₄, 3PbO·PbSO₄·H₂O, 4PbO·PbSO₄),

and mixtures thereof. Different materials may be used in connection with the lead-containing paste composition, with the present invention not being restricted to any particular materials or mixtures (added fibers, or other constituents). These materials may be employed alone or in combination as determined by numerous factors, including for example, the intended use of the battery **100** and the other materials employed in the battery.

The negative plate **106** may be composed of a metal (e.g., lead or lead alloy) grid with a spongy lead active material or paste **130** thereon. The negative paste **130** may, in a preferred embodiment, be substantially similar to the positive paste **128** but may also vary. Example lead-containing compositions which may be employed in the negative paste **130** include but are not limited to finely-divided elemental Pb, PbO (“litharge” or “massicot”), Pb₃O₄ (“red lead”), PbSO₄ (“Lead sulfate” with the term “PbSO₄” being defined to also include its associated hydrates, and basic sulfates: 1PbO·PbSO₄, 3PbO·PbSO₄·H₂O, 4PbO·PbSO₄), and mixtures thereof. In addition, the negative active material **130** may also contain fiber and/or “expander” additives which may help maintain the active material structure and improve performance characteristics, among other things. Different materials may be used in connection with the lead-containing paste composition, with the present invention not being restricted to any particular materials or mixtures (added fibers, or other constituents). These materials may be employed alone or in combination as determined by numerous factors, including for example, the intended use of the battery **100** and the other materials employed in the battery.

According to one or more examples of embodiments, the active material or paste **128** and/or **130** may have an improved composition or recipe over traditional AGM batteries. Preferably, the active material composition or recipe provides a changed, or improved, charge acceptance performance and/or efficiency (e.g., dynamic charge acceptance) over existing AGM batteries while also maintaining or improving CCA (Cold Cranking Amps at -18 degrees C.) performance and cycle life performance. In some examples, the dynamic charge acceptance may be greater than 2 times the performance of existing AGM batteries. In fact, as will be discussed in greater detail below, relative to existing commercial batteries on the market today, against some current commercial batteries the battery disclosed herein may perform up to 5 times better (e.g., see FIG. **13**; 0.79/0.13=5x) and against other current commercial batteries may perform at least 2 times better (e.g., see FIG. **13**; 0.79/0.326=2x). The current industry average is around 0.3 A/Ah for an EN50342 DCA test. In comparison, the battery **100** disclosed herein may perform around 0.78-0.79 A/Ah with the various improvements described herein (see FIG. **13**).

Lead oxide is used to make a paste which is spread onto the metal grids. After chemical conversion the paste becomes the active material. The lead oxide is made by reacting the pure lead metal with oxygen in the air. In various examples, the particle size distribution of the leady oxide used to make the active material pastes **128** and/or **130** may be closely controlled. That is, a specific or preferred particle size distribution may be used for the intended purposes. In some examples, the positive electrochemically active material may have a positive oxide having a bimodal particle size distribution of leady oxide (see FIG. **9**). For example, the positive oxide may be composed of an oxide with a particular bimodal particle size distribution with peaks at 0.87-1.2 um and 2.0-4.0 um oxide, for example. In

one or more particular examples, the bimodal oxide distribution may range from 0-90% of a first oxide type and 0-90% of a second oxide type (i.e., having differing sizes), and a remainder, red lead; and more preferably, a bimodal oxide distribution which may range from 20% to 50% of a first oxide type and 20% to 50% of a second oxide type, and a remainder red lead. Differences in particle sizes lead to a more efficient packing and may impart superior properties to the eventual active material. While various examples are described, one of skill in the art will appreciate modifications can be made for the intended purposes without departing from the overall scope of the present invention. Note, the current standard method in the art is to use either a thermal mill oxide with a particle size distribution (PSD) $D_{50} \Rightarrow 2.0$ μm , or an attrition mill oxide with PSD $D_{50} \Rightarrow 0.7$. PSD may be measured by Helios laser particle size analyzer. These parameters are indicative only and dependent upon machine type and processing conditions. For example, various methods are known for making leady oxide, such as for example, Barton Pot method (thermal) and Ball Mill method (attrition). The particle size distribution of the oxide that results from the two processes may be different. For instance, a Barton Pot process may produce a peak D_{50} distribution at between 2.0 and 4.0 μm (for example) (see FIG. 10), while Ball Mill oxide may have a D_{50} distribution between 0.7 μm and 1.2 μm (for example) (see FIG. 11).

In one example, the negative active material **130** or negative mass may also or alternatively be improved. For example the negative mass recipe may include an improved expander, or other alternatives which accomplish the foregoing objectives. In various examples, the negative mass may include one or more additives. In this regard, improved AGM battery charge acceptance of the negative plate **106** may be accomplished by using individually or in combination (e.g., as an addition to the negative paste **130** or included in the negative paste mass) one or more of the following:

One or more carbons (carbonaceous materials), such as but not limited to, high surface area conductive carbon black with specific properties for the intended purposes, and/or natural or synthetic graphite, and/or carbon nanotubes, and/or graphene, and/or activated carbon, and the like at dosing levels from 0.01 to 1.0 weight percent (wt %), and more preferably may be from 0.09 to 0.9 wt %; for example: dosing levels for some components, e.g., carbon nanotubes, are very low and may be from 0.01 to 0.1 wt %, while activated carbons and graphites may approach 1.0 wt % dosage level;

One or more organic expanders, such as but not limited to, dispersant-type materials, including for example, synthetic (e.g., naphthalene sulfonate condensate, phenolic sulfonate condensate molecules) and/or organic or non-synthetic materials derived from, for example wood chemicals (e.g., lignin, lignosulfonates, humates or humic acid (and ionic salts thereof, i.e., sodium lignosulfonate)), among others at dosing levels from 0.01 to 1.0 wt %, and more preferably may be from 0.1 to 0.5 wt %; and/or

Barium sulfate, which may be fine particle size barium sulfate (e.g., 0.1 micron, 0.7 micron (μm , μm)) at a wt % dosing level ranging from 0.5 to 2.0 wt %, and more preferably may range from 0.7 to 1.25 wt %, and even more preferably may range from 0.90 to 1.10 wt %.

Alternative negative mass recipes may also be provided which accomplish the objectives described herein.

Referring to the foregoing, carbon nanotubes and the like may maintain a conductive matrix in the active material, thereby improving performance, especially in regards to micro-cycling as used in micro-hybrid and start-stop applications. In other examples, surface oxidized graphite, as well as conductive carbon black with high surface area and high structure also provide improved performance. According to further examples of embodiments, one or more carbons may be combined (by weight percent) such as a conductive large particle carbon and a smaller particle carbon form (e.g., allotrope).

Advantageously, fine particle barium sulfate produces a greater number of small lead sulfate crystals during discharge. In turn, these small lead sulfate crystals dissolve easier during charge than large lead sulfate crystals, leading to an improvement in charge acceptance.

In addition to the foregoing, the negative plate **106** may also have the advantageous feature of resisting the buildup of dense passivating lead sulfate. For example, for the negative plate **106**, the charge/discharge reaction involves the conversion of lead to lead sulfate (discharge) and the lead sulfate to lead (recharge). The process proceeds via a dissolution-precipitation mechanism. Components that influence either dissolution or precipitation can influence performance. For instance: (1) fine particle barium sulfate is believed to provide more nucleation sites for fine lead sulfate deposition and dissolution; (2) organic expanders are surface active molecules which impede the deposition of lead as a non-porous layer, the lead is deposited as high surface area sponge lead in the presence of organic expanders, i.e., organics prevent sintering of the lead electrode; (3) the carbon conductive network allows better utilization of the inner part of the active material, so reactions are not limited to the surface of the plate where mass transport is easiest. The foregoing assists in mitigation the lead-sulfate buildup on the surface of plates which prevents access to the interior of the active mass.

The negative plate **106** may also have the advantageous feature of, in one or more examples, maintaining functionality for the life of the battery **100**. For instance, the negative plate **106** may have low gassing and low water consumption, enabling, for example, longer useful service life in a vehicle **102** during idle-stop-start operation. As a non-limiting example, the surface active properties of the components (e.g., barium sulfate, organic expander, and carbon additive) may change the electrochemical potential of the active material surface, thereby, changing the rate of fundamental reactions such as gas evolution. The additives may act to change the electrochemistry, changing the rate or potential at which gas is produced. Lead acid batteries produce gas on charging—hydrogen from the negative and oxygen from the positive—the rate of gas production (and water loss) can be modified by the paste additives. Components with a high surface area can lower the current density, while carbons may have a capacitive effect, and organic materials may bind to surfaces preventing access to the surface and thus raising the potential at which gas is evolved.

In addition to the foregoing, in one or more examples of embodiments, the pasted plates **104** and/or **106** (with or without surface scrim) may be imprinted, or have an imprint on the surface, to provide for example a plurality of grooves such as disclosed in United States Patent Publication No. 2015/0104715, the entire contents of which is hereby incorporated by reference in its entirety. As disclosed in said publication, the imprint or grooves may assist in electrolyte flow and air removal, among other benefits. In one or more examples, a “waffle” pattern surface treatment **150** of vari-

ous grooves, such as shown in FIG. 12, may be provided on a plate surface 148, such as but not limited to, the positive plate 104. A plate surface treatment may also include a “riffle” pattern on the negative plate 106 (or in some embodiments the positive plate 104). In one or more examples, a pasting paper 132 may also be used, e.g. added to a plate 104, 106.

As indicated, separator material 108 may be provided between each positive plate 104 and negative plate 106. The separator 108 may be an absorbent glass mat or AGM, and in one or more examples of embodiments may be wrapped around a portion of, or interleaved with/provided between one (or both) of the positive and negative plates 104, 106. A single or double layer of AGM 108 may be employed. For example, a separator may be provided on the positive plate and an AGM 108 may also be employed with the positive/negative plates. The absorbent glass mat 108 may be constructed similar to and/or of a similar material to a traditional absorbent glass mat separator, including thin glass fibers woven into a mat (or more commonly non-woven deposited fibers). However, variations thereon which accomplish the purposes disclosed herein may also be acceptable. In one or more examples of embodiments, a thin glass scrim or mat may be provided on the positive plate.

An electrolyte, which is typically sulfuric acid, may be included in the battery 100. In various examples, the electrolyte may include one or more metal ions. To this end, the sulfuric acid electrolyte may be a sulfuric acid solution including one or more metal sulfates. More specifically, in one example, a specific optimized combination of one or more of the following may be selected to accomplish the improved battery performance described herein: soluble metal sulfates from elements Al, Mg, Na, K, Li, Zn, and the like. The current standard in industry is a Na at 10-15 g/liter. The electrolyte described herein preferably may have a combination of one or more of the following: Mg, Mg+Na, Al, Al+Na, and/or Zn, Zn+Na, ranging from 0 g/liter to 10 g/liter for each, with a total not greater than 15 g/liter. Generally, the mechanism used is the common ion effect (e.g., sulfate is common). This impedes or permits the dissolution of lead sulfate during charge, depending on the amount of the salt already in the electrolyte. A secondary mechanism may also be employed in which the metal ion is deposited onto the negative electrode surface where it acts to change the electrochemical potential. The ability to accept charge is enhanced, and in some examples is enhanced by about 50% above a standard battery. While specific examples are discussed above, variations thereon may also be acceptable for the purposes provided.

In one or more alternative examples of embodiments, various additional/alternative elements of the AGM lead-acid battery may be improved or changed to achieve the desired performance, including but not limited to changes in separator composition, changes in polymer for the battery container 114, and/or other new or alternative components.

Accordingly, a battery 100 as described in one or more examples of embodiments herein includes a novel negative paste recipe and/or paste components, additives to electrolyte, a scrim surface pattern, and radial, fully framed positive and negative grids of the types described herein. In some examples of embodiments, the foregoing is used in association with an absorbent glass mat. However, it is contemplated that a lead acid battery having one or more of the foregoing components may be provided without an absorbent glass mat, and instead with a separator.

More specifically, a lead-acid storage battery 100 is disclosed. The battery includes a container with a cover. The

container includes one or more compartments. One or more cell elements are provided in the one or more compartments, the one or more cell elements include a positive plate, the positive plate having a positive grid and a positive electrochemically active material on the positive grid; a negative plate, the negative plate having a negative grid and a negative electrochemically active material on the negative grid, wherein the negative electrochemically active material comprises fine particle barium sulfate and an organic expander; and a separator between the positive plate and the negative plate. An electrolyte is provided within the container. One or more terminal posts extend from the container or the cover and electrically are coupled to the one or more cell elements. In some examples of embodiments, an absorbent glass mat may be provided in addition to the separator or in place of the separator. A scrim may also be provided, as well as an imprinted pattern on a plate and/or scrim surface. In some examples of embodiments, a carbon may also be provided in the negative electrochemically active material. A bimodal particle distribution of oxide may also be provide in the active material, such as on the positive plate.

According to one or more examples of embodiments, a battery 100 is disclosed herein, which as a result of one or more of the features described, may have endurance (e.g., cycling, water consumption, service life under the hood, and maintained start-stop functionality). The battery 100 may also have high charge acceptance, which may be dynamic and/or static charge acceptance, as well as at partially charged states. The battery 100 may also have high current performance, which may be maintained for engine starting, including cold starts and warm starts. The battery 100 may further have high current performance, which may be beneficial for, among other things, power assist on launch of a vehicle 102. The battery 100 may also have high capacity, which may be useful for, among other things, maintaining vehicle 102 systems during a stop event in a start-stop operation (e.g., for lighting, AC, onboard computers, and other vehicle systems).

Advantageously, a battery 100 having the features described herein has improved performance, and provides sustainable and fast re-chargeability and consistent cycling performance over time. The active material composition or recipe provides a changed, or improved, charge acceptance performance and/or efficiency (e.g., dynamic charge acceptance) over existing AGM batteries. Thus, a battery 100 having one or more of the features described herein may be capable of delivering enhanced charge acceptance when operated in a partially discharged state, suitable for start-stop operation. The battery 100 having one or more of the features described herein may also provide enhanced dynamic charge acceptance suitable for use in regenerative braking, as well as start-stop operation. The battery 100 may also have high partial state of charge cycling performance (endurance) capable of maintaining start-stop functionality of a vehicle 102 for a significantly longer life than conventional batteries. The battery 100 may also have good cold cranking capacity and under the hood life, as well as enhanced ISS (Idle Start Stop) performance.

EXAMPLES

The following Examples are an illustration of one or more examples of embodiments of carrying out the invention and are not intended as to limit the scope of the invention.

Example 1

In one or more examples of embodiments, charge acceptance, and in particular, dynamic charge acceptance, of the

battery 100 described herein was compared relative to various industry standards. A number of batteries were assembled including the various components described herein. In particular, in the illustrated example, the particular batteries tested against various industry standard examples 5 included plates, such as negative plates, with a fine particle barium sulfate, an organic expander, and a conductive carbon. The plates of the sampled batteries, both positive and negative, also included PowerFrame® grids available from Johnson Controls, PLC (Milwaukee, WI), a scrim, and 10 a surface treatment on the plate.

As can be seen in FIG. 13, which illustrates a Dynamic Charge Acceptance Test (DCA) performed according to industry standard, the battery 100 described herein performed significantly better than the various example standard batteries. As can be seen, the test results show batteries 15 with a DCA greater than 0.6 A/Ahr and in several instances greater than 0.7 A/Ahr. These results show performance ranging from 2 to 5 times a standard battery, and may range from 2 to 3 times an industry average for dynamic charge acceptance.

While specific examples are shown, one of skill in the art will recognize that these are examples only and variations thereon may be made without departing from the overall scope of the present invention.

As utilized herein, the terms “approximately,” “about,” “substantially,” and similar terms are intended to have a broad meaning in harmony with the common and accepted usage by those of ordinary skill in the art to which the subject matter of this disclosure pertains. It should be understood by those of skill in the art who review this disclosure that these terms are intended to allow a description of certain features described and claimed without restricting the scope of these features to the precise numerical ranges provided. Accordingly, these terms should be 35 interpreted as indicating that insubstantial or inconsequential modifications or alterations of the subject matter described and claimed are considered to be within the scope of the invention as recited in the appended claims.

It should be noted that references to relative positions (e.g., “top” and “bottom”) in this description are merely used to identify various elements as are oriented in the Figures. It should be recognized that the orientation of particular components may vary greatly depending on the application in which they are used. 45

For the purpose of this disclosure, the term “coupled” means the joining of two members directly or indirectly to one another. Such joining may be stationary in nature or moveable in nature. Such joining may be achieved with the two members or the two members and any additional intermediate members being integrally formed as a single unitary body with one another or with the two members or the two members and any additional intermediate members being attached to one another. Such joining may be permanent in nature or may be removable or releasable in nature. 55

It is also important to note that the construction and arrangement of the system, methods, and devices as shown in the various examples of embodiments is illustrative only. Although only a few embodiments have been described in detail in this disclosure, those skilled in the art who review this disclosure will readily appreciate that many modifications are possible (e.g., variations in sizes, dimensions, structures, shapes and proportions of the various elements, values of parameters, mounting arrangements, use of materials, colors, orientations, etc.) without materially departing from the novel teachings and advantages of the subject matter recited. For example, elements shown as integrally 65

formed may be constructed of multiple parts or elements show as multiple parts may be integrally formed, the operation of the interfaces may be reversed or otherwise varied, the length or width of the structures and/or members or connector or other elements of the system may be varied, the nature or number of adjustment positions provided between the elements may be varied (e.g. by variations in the number of engagement slots or size of the engagement slots or type of engagement). The order or sequence of any process or method steps may be varied or re-sequenced according to alternative embodiments. Other substitutions, modifications, changes and omissions may be made in the design, operating conditions and arrangement of the various examples of embodiments without departing from the spirit or scope of the present inventions. 15

While this invention has been described in conjunction with the examples of embodiments outlined above, various alternatives, modifications, variations, improvements and/or substantial equivalents, whether known or that are or may be presently foreseen, may become apparent to those having at least ordinary skill in the art. Accordingly, the examples of embodiments of the invention, as set forth above, are intended to be illustrative, not limiting. Various changes may be made without departing from the spirit or scope of the invention. Therefore, the invention is intended to embrace all known or earlier developed alternatives, modifications, variations, improvements and/or substantial equivalents. 25

The technical effects and technical problems in the specification are exemplary and are not limiting, it should be noted that the embodiments described in the specification may have other technical effects and can solve other technical problems.

The invention claimed is:

1. A lead-acid storage battery comprising:

a container with a cover, the container including one or more compartments;

one or more cell elements in the one or more compartments, the one or more cell elements comprising:

a positive plate, the positive plate having a positive grid and a positive electrochemically active material on the positive grid;

a negative plate, the negative plate having a negative grid and a negative electrochemically active material on the negative grid, wherein the negative electrochemically active material comprises fine particle size barium sulfate, an organic expander, and conductive carbon, the conductive carbon comprising activated carbon and 0.01 to 0.1 percent by weight carbon nanotubes; and

an absorbent glass mat separator between the positive plate and the negative plate;

electrolyte within the container; and

one or more terminal posts extending from the container or the cover and electrically coupled to the one or more cell elements. 50

2. The lead-acid storage battery of claim 1, wherein the negative electrochemically active material further comprises one or more carbons are selected from the group consisting of high surface area conductive carbon black, natural or synthetic graphite, and graphene. 60

3. The lead-acid storage battery of claim 1, wherein the electrolyte comprises a sulfuric acid solution including one or more metal sulfates, wherein the metal sulfates are soluble metal sulfates selected from the group consisting of elements Al Mg, Na, K, Li, and Zn. 65

4. The lead-acid storage battery of claim 1, wherein at least one of the positive electrochemically active material

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and the negative electrochemically active material has a bimodal particle size distribution of oxide.

5. The lead-acid storage battery of claim 1, wherein the organic expander is a naphthalene sulfonate.

6. The lead-acid storage battery of claim 1, further comprising an additional separator between the positive plate and the negative plate.

7. The lead-acid storage battery of claim 1, further comprising a pasting paper.

8. The lead-acid storage battery of claim 1, wherein the organic expander is a wood chemical.

9. A lead-acid storage battery comprising:

a container with a cover, the container including one or more compartments;

one or more cell elements in the one or more compartments, the one or more cell elements comprising:

a positive plate, the positive plate having a positive grid and a positive electrochemically active material on the positive grid;

a negative plate, the negative plate having a negative grid and a negative electrochemically active material on the negative grid, wherein the negative electrochemically active material comprises fine particle size barium sulfate, an organic expander, and conductive carbon, the conductive carbon comprising activated carbon and 0.01 to 0.1 percent by weight carbon nanotubes; and

a separator between the positive plate and the negative plate;

electrolyte within the container; and

one or more terminal posts extending from the container or the cover and electrically coupled to the one or more cell elements.

10. The lead-acid storage battery of claim 9, wherein the negative electrochemically active material further comprises one or more carbons are selected from the group consisting of high surface area conductive carbon black, natural or synthetic graphite, and graphene.

11. The lead-acid storage battery of claim 9, wherein the electrolyte comprises a sulfuric acid solution including one or more metal sulfates, wherein the metal sulfates are soluble metal sulfates selected from the group consisting of elements Al, Mg, Na, K, Li, and Zn.

12. The lead-acid storage battery of claim 9, wherein at least one of the positive electrochemically active material and the negative electrochemically active material has a bimodal particle size distribution of oxide.

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13. The lead-acid storage battery of claim 9, wherein the organic expander is a wood chemical.

14. The lead-acid storage battery of claim 9, wherein the organic expander is a naphthalene sulfonate.

15. The lead-acid storage battery of claim 9, further comprising an additional separator between the positive plate and the negative plate.

16. The lead-acid storage battery of claim 9, further comprising a pasting paper.

17. A lead-acid storage battery comprising:

a container with a cover, the container including one or more compartments;

one or more cell elements in the one or more compartments, the one or more cell elements comprising:

a positive plate, the positive plate having a positive grid and a positive electrochemically active material on the positive grid;

a negative plate, the negative plate having a negative grid and a negative electrochemically active material on the negative grid;

wherein the negative electrochemically active material comprises one or more carbons, fine particle size barium sulfate, and one or more organic expanders, wherein the one or more carbons are activated carbon and 0.01 to 0.1 percent by weight carbon nanotubes; and

an absorbent glass mat separator between the positive plate and the negative plate;

electrolyte within the container, wherein the electrolyte comprises a sulfuric acid solution including one or more metal sulfates, wherein the metal sulfates are soluble metal sulfates selected from the group consisting of elements Al, Mg, Na, K, Li, and Zn; and

one or more terminal posts extending from the container or the cover and electrically coupled to the one or more cell elements.

18. The lead-acid storage battery of claim 17, wherein the one or more carbons are selected from the group consisting of high surface area conductive carbon black, natural or synthetic graphite, and graphene.

19. The lead-acid storage battery of claim 17, wherein at least one of the positive electrochemically active material and the negative electrochemically active material has a bimodal particle size distribution of oxide.

20. The lead-acid storage battery of claim 17, wherein the one or more organic expanders are a naphthalene sulfonate.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 11,870,096 B2
APPLICATION NO. : 17/882035
DATED : January 9, 2024
INVENTOR(S) : Frank-Thomas Johns et al.

Page 1 of 1

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

On the Title Page

On Page 2, in Item (57), under "ABSTRACT", in Column 1, Line 1, delete "extend," and insert -- extend --, therefor.

In the Specification

In Column 1, Line 3, delete "CROSS-REFERENCE. TO" and insert -- CROSS-REFERENCE TO --, therefor.

In Column 4, Line 61, delete "Dumber" and insert -- number --, therefor.

In Column 5, Line 67, delete "1PbO·PbSO₄, 3PbO·PbSO₄·H₂O, 4PbO·PbSO₄)," and insert -- 1PbO.PbSO₄, 3PbO.PbSO₄.H₂O, 4PbO.PbSO₄), --, therefor.

In Column 6, Line 19, delete "1PbO·PbSO₄, 3PbO·PbSO₄·H₂O, 4PbO·PbSO₄)," and insert -- 1PbO.PbSO₄, 3PbO.PbSO₄.H₂O, 4PbO.PbSO₄), --, therefor.

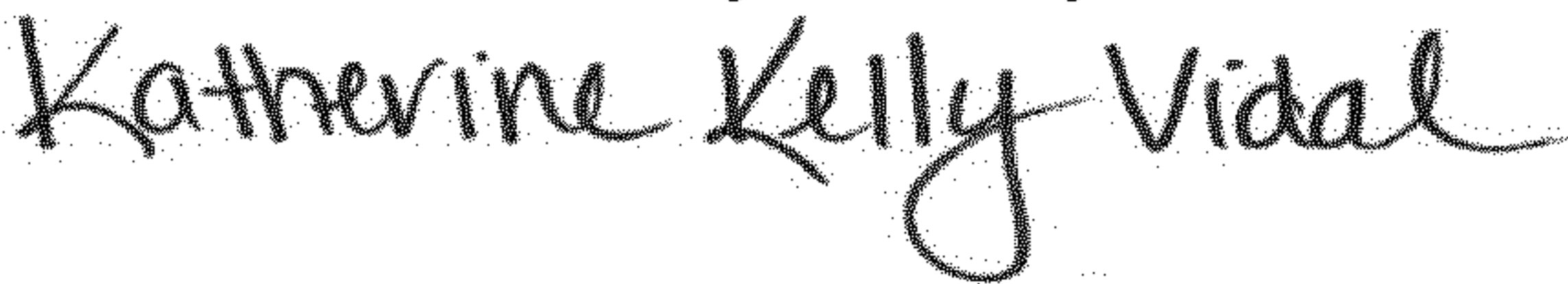
In Column 9, Line 38, delete "glitter" and insert -- g/liter --, therefor.

In Column 12, Line 29, delete "limiting, it" and insert -- limiting. It --, therefor.

In the Claims

In Column 12, Line 65, Claim 3, delete "Al Mg," and insert -- Al, Mg, --, therefor.

In Column 14, Line 46, Claim 20, delete "sultanate." and insert -- sulfonate. --, therefor.

Signed and Sealed this
Fourteenth Day of May, 2024

Katherine Kelly Vidal
Director of the United States Patent and Trademark Office